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Final REPORT

Growth and Characterization of Large Diameter CdNzTe Crystals

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Abstract

The report summarizes the activities during the whole contract period. Parts of the results were presented in Progress Reports No.1 and 2 and will not be repeated in detail. The goal of the effort was aimed to test the middle-pressure setup after completion and modification. Several boules were grown, wafers with dimensions $10x10mm^2$ were fabricated and delivered to NVESD. New wafers with dimensions $10x10mm^2$ and $20x20mm^2$ are delivered in parallel to this report. As was reported in Progress Report No.2 additional annealing approach has been developed in order to decrease the size of inclusions to the size acceptable for MBE growth for cases, where inclusion formation was not suppressed during the growth. The main goal was to look for such annealing conditions, when inclusion size and density is decreased and the crystal microstructure is not damaged during the annealing process. A future outlook based on the results of a longer-term effort in CZT growth and substrate fabrication in the Institute of Physics, Charles University in Prague is presented.

Introduction

During this contract period the growth setup was completed by a closed cycle water cooling sytem. The purpose was to stabilize the temperature of the water cooling the growth furnace and to decrease this way fluctuations of temperature during the growth. Also situations, when the water supply was stopped due to breaks or repairs outside the institute can be avoided.

A complete description of the growth setup including the programs for temperature control will be given . Although part of this information was provided in the last contract periods, it seems reasonable to summarize it after the whole building activity was finished.

Several growth runs were performed. The results will be described .

The growth setup

An electronic control system has to be designed to control both temperature and internal pressure of two zones (CdZn)Te crystal growth furnace. The schematic drawing of the control setup can be seen on Fig. 1. The furnace was built inside of the stainless steel water cooled, high pressure containment (possible pressures can reach up to 50 bars). Its cooling water circulation system is closed and thermostated by air cooled heat pump. The synthesized polycrystalline CdZnTe is placed inside of the evacuated silica glass ampoule. There are two independent heating elements to control the internal temperature gradient during the crystal growth process. Two high performance PID electronic controllers/setpoint programmers are used in the setup, one for the temperature and the latter for the containment internal pressure control. Both controllers enable free software wiring of all process variables and parameters.

The temperature controller is configured as two-loop control system. Cascade control can be applied as an advanced control technique to get the best temperature setpoint stability for one loop (see Fig.1). This enables long time constant of the furnace to be controlled with the fastest possible response of the control system to the temperature profile perturbation caused by occurring exothermic processes and it also increases the heating elements lifetime substantially. Cascade control approach improves effectively the time lag between the temperature change of the heating element and the ampoule. This control electronics wiring enabled us to drive both heating elements of the furnace more or less independently. However, one must be aware of influencing the temperature stability, when the temperature gradient is changed rapidly. The temperature stability of both zones of the furnace is better than 0.01^0 C. Phase angle firing thyristor units are driven by the controller output to control the heating power. Three Pt/PtRh10 inconel coated thermocouples are used to monitor the temperature inside of the containment very precisely. The main control thermocouples are close to the ampoule and the auxiliary one is close to the heating element. Extremely high sensitive differential thermocouple is also placed below of the ampoule to monitor starting and end of the crystallization process. This signal is collected by using a high precision digital multimeter equipped with 8 channels analog scanner.

The temperature value in the furnace upper zone above 800^0 C causes substantial nonlinear increasing of the ampoule internal pressure above 1 bar originating from the Cd

evaporation process. Nascent overpressure must be immediately compensated by appropriate filling of the stainless steel containment volume with an inert gas (Argon) to avoid the ampoule damaging during the crystal growth process. This process is illustrated on Fig. 2. Argon pressure in the containment is controlled by the pressure controller, which is configured in single loop control setup with 0 to ± 100% opening of the control output. It drives two proportional high-grade electromagnetic valves for the flow control of the containment filling by Argon in the interval from 1 to 5 bars. The positive output means pressured Argon input proportional valve opening while the negative output is opening the outlet proportional valve. This setup ensured that only one valve could be opened during the pressure control so that Argon consumption can be optimized. Supplementary passive flow control needle valves are used to limit the maximum flow of the gas. It allows time constants of the internal pressure changes in the containment to be controlled. An absolute value pressure gauge sensor is mounted inside of the containment. Current loop (4 – 20 mA) is used to transmit instantaneous pressure value to the controller. Highly sensitive Linear Differential Variable Displacement (LVDT) sensor is attached to the ampoule surface to monitor its inflation due to possible Cd vapors overpressure. Displacement detection sensitivity is better than 1 μm and its signal is considered to be a critical condition for switching off heating element of Cd zone in case of emergency. The pressure controller/setpoint programmer enables to control Argon filling profile during the process. The internal pressure stability without fast deviations is a very important assumption substantially influencing the crystal growth process. Manual tuning of PID parameters by using Ziegler-Nichols algorithm has been necessary to get over big flow control nonlinearities resulting from the dependence of the valve opening characteristics on the internal pressure variations. The pressure stability interval can reach up to 50 mbar. Three separate sets of PID parameters are assigned to specified pressure intervals. The pressure setpoint value profile during the crystal growth process can be preprogrammed to the setpoint programmer; however it is usually calculated by the control computer on basis of analysis the temperature data taken from Cd furnace zone by the temperature controller and the digital multimeter.

RS 485 two wire current loop serial communication bus is used for the data exchange and computer control of the furnace electronics setup. Digital multimeter scanner is simultaneously used for recording of various safety and process monitoring signals. It communicates with the control computer by using GPIB bus.

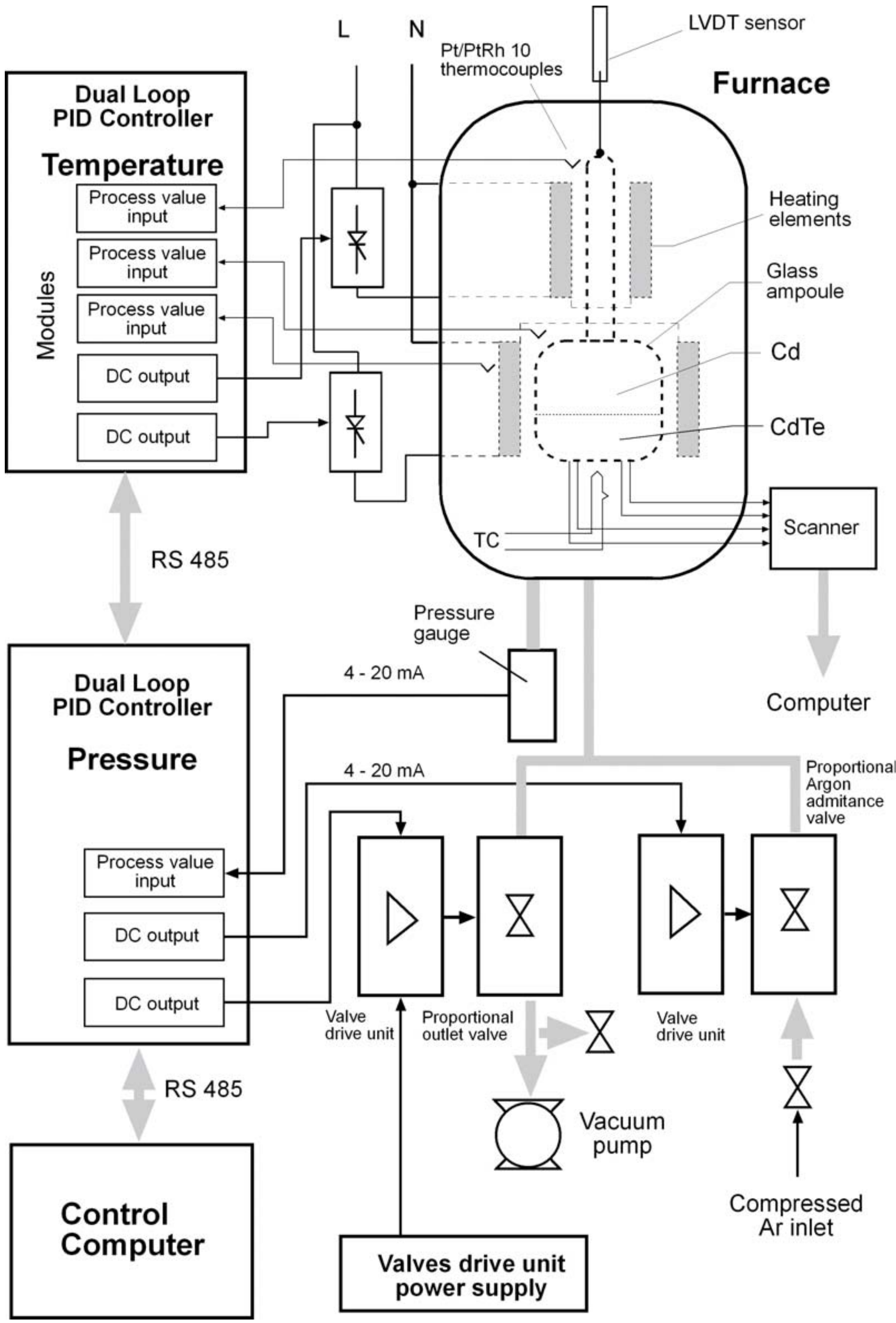

L
N
LVDT sensor
Pt/PtRh 10
thermocouples
Furnace
Dual Loop
PID Controller
Temperature
Modules
Process value input
Process value input
Process value input
DC output
DC output
Heating elements
Glass ampoule
Cd
CdTe
TC
Scanner
RS 485
Pressure gauge
Computer
4 - 20 mA
Dual Loop
PID Controller
Pressure
4 - 20 mA
Proportional
Argon
admitance
valve
Process value input
DC output
DC output
Valve drive unit
Proportional outlet valve
Valve drive unit
RS 485
Vacuum pump
Control Computer
Valves drive unit power supply
Compressed Ar inlet

Fig.1

The temperature profile in the furnace during the crystal growth process is preprogrammed in the temperature controller. The main task of the computer program is to control Ar pressure in the stainless steel containment surrounding the ampoule and the furnace. The other function of the program is data acquisition (and storage) for the documentation of the process.

After program invocation, one can perform certain modifications in the configuration of measuring apparatus, e.g. to enable additional digital multimeter input channels and to select its measuring modes. When the "Start" button is pressed, the program activity begins. From this moment, the changes in the configuration are not possible onwards, but some parameters are still changeable. The program runs in an infinite loop. Every 10 seconds the *PressureControl* procedure is called, and after three such cycles, the *DataMeasurements* procedure is called. With the exception of the most of the *PressureControl* procedure, the Windows messages (like button clicks) are processed, and therefore the program can react immediately to button clicks in the forms.

The *PressureControl* procedure is the most important part of the program. It performs the measurements of T1 (upper zone) and T3 (lower zone) temperatures to compute the approximate cadmium pressure in the ampoule and then it sends the required setpoint value to the pressure controller to adjust Ar pressure in the containment. The Cd pressure P_{Cd} is calculated as $P_{Cd} = a \cdot f(\min(T_1, T_3)) + b$, where *f(T)* is the analytical function published in Ref.[10]. The analytical function is supposed to be valid up to 920^0 C. As we need to extrapolate this dependence up to 1100^0 C, two empirical coefficients *a* and *b* were introduced to improve the agreement with the real situation. Their values were estimated during the previous experiments. Calculated P_{Cd} (in mbar) is rounded to the nearest integer value and sent to the pressure controller. A test of four sensors (temperature and Argon pressure) is performed by calling corresponding controller functions at the subroutine entry. If any sensor is broken, or if any of the measured values T1 or T3 are out of prescribed interval, or if they differ from the previous values by more than 50^0 C, an error message ocurres. If three consecutive errors have occurred, the experiment is stopped (both controllers are switched to "Hold" state, where the temperature and the pressure remains without changes).

In the *DataMeasurements* procedure, all experimental data are read, displayed and stored to a disk file. Besides this data file, another file "History.txt" is used to log all important situations

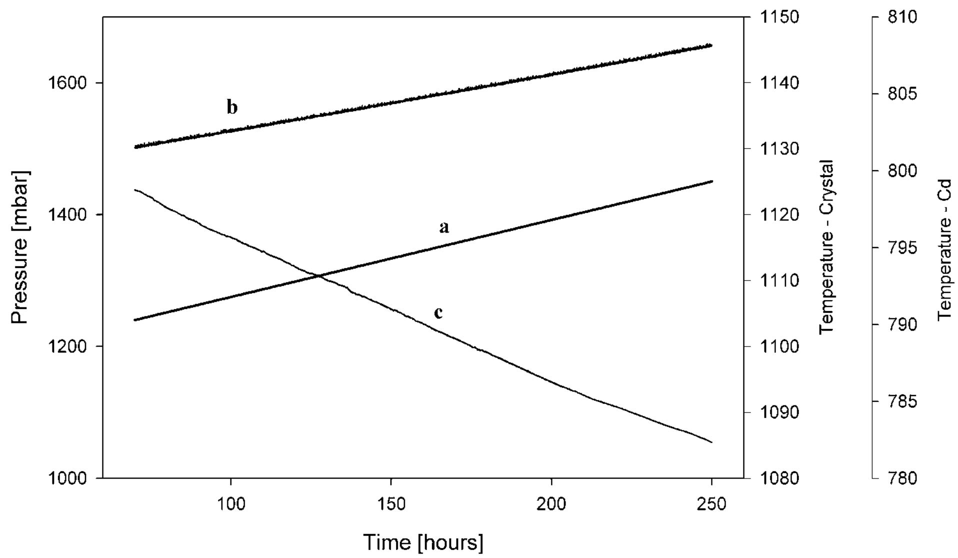


Fig.2

during the process running, e.g. start and stop times, changes of controllers state (either entered in the program or manually from the controller front panel keypad), all warning and error messages, etc.

The computer program was written in Microsoft Visual Basic 6, it has almost 3000 lines of code. During the program run, the *Main* form (see Fig. 3) is permanently displayed, another 3 forms can be opened and closed arbitrarily. In the *ControlerControl* form, one can enter new *SetPoint* values, or to change the controller state, or to switch between the internal temperature profile programs. In the *Table* form, all data measured in *DataMeasurements* procedure are shown numerically. Finally, the *Plot* form shows a plot of 4 important quantities, each having its own vertical axis. Both horizontal axis (time) and all four displayed quantities independently can be completely controlled with zoom and shifts. When the *Plot* form is opened, the new values of all four quantities are added into the plot in real time. When operator is watching the older values, real-time mode is turned off automatically. It is turned on again by a click on the "Refresh" button, or after some time elapses.

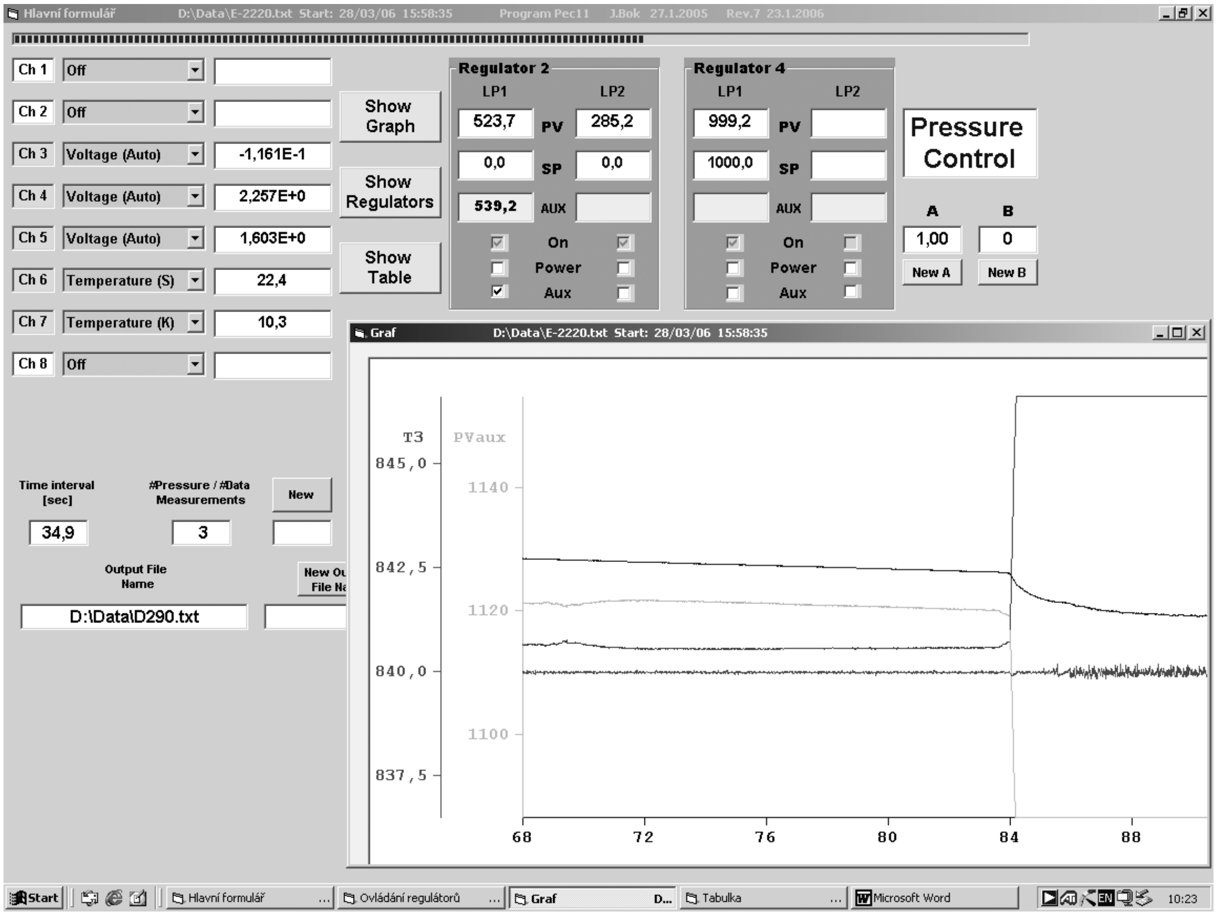


Fig.3

Crystal growth

Six crystal growth experiments were done after modification of the crystal growth setup described in the final report to the previos project. The temperature gradient and growth speed were varied in order to find optimal growth conditions. The main studied parameters were – the size of the single crystalline grains, transmissivity, X-ray rocking curves FWHM, presence of inclusions. The list of the experiments is given in Table I.

No.	Temp. Gradient (K/cm)	Cooling speed (K/hour)	Cd pressure (mbar)	T_{max} (K)
1	1.8	0.33	1954	1120
2	1.8	0.15	1790	1116
3	1.8	0.2	1663	1120
4	3.2	0.22	1555	1120
5	0.9	0.11	1872	1125
6	0.9	0.11	1620	1125
7	2	0.2	1200	1120

The main problem we were facing was a small size of the grains in the first experiments, which does not allow to produce substrates of reasonable dimensions and to characterize other properties. In order to remove this problem the temperature gradient at the growth interface was kept constant and the cooling speed was varied. This approach did not lead to a substantial enlargement of the size of the grains. In the fourth experiment the temperature gradient was increased to 3.2 K/cm in comparison to 1.8K/cm. Also this experiment resulted in a crystal with a large number of small grains. In the fifth experiment both the temperature gradient and the cooling speed were substantially decreased. Also the maximum temperature of overheating was increased to to 1125˚C. The reason, while we were working with a higher gradient in the first experiments was, that in theory a larger gradient leads to a decreased supercooling, which should result in a single crystalline, good quality material. The experiment No.5 resulted in a single crystalline material, where two large grains were filling in practically the whole volume of the crucible. Experimental conditions found in this experiment were repeated in the next growth run. This run was completed recently. Visual observation of the grain structure showed, that several large graines fill in the whole volume of the boule. The positive tendency in applicion of small gradients combined with a small cooling speed seems to be present. These experimental conditions will be repeated in the next growth runs.

Due to the above mentioned problems with the size of single crystals grown at high Cd pressure one crystal was prepared under a lower Cd pressure (~1.2atm). The resulting grain structure was favorable. The transmissivity at 10μm was low. Inclusions with a typical size to 6

μm was also present. This crystal was treated by annealing in order to improve the transmissivity and to decrease the inclusion size. The results will be presented in the next section.

The growth of CZT proves to be very difficult. Although there is some general theoretical knowledge about crystal growth processes, these are difficult to apply, beacuse apparently many , in part not well known factors influence the final result. Therefore each furnace requires to be tested and optimum growth condition seems to be at least partially furnace-specific. The effort must be based on a large amount of purely empirical knowledge, which is very time consuming especially in a small laboratory, where only one furnace is available.

The developed setup enables very good control of Cd pressure during the growth process, provides a very good temperature control and is also important from safety regions, because in case of explosion the contamination is limited to the inner part of the steel container. Initial growth experiments indicated two main results of growth at higher pressures – very good transmissivity (>60%) and small amount of inclusions. Based on the results of evaluation of the quality of wafers submitted to NVESD during the contract period reported in Progress report No.2, the assumption of inclusion reduction appeared to be overoptimistic. A more detailed investigation of the boules has shown, that the region without inclusions is limited to a severall mm thick region, which is in direct contact with Cd vapors (the upper surface and the walls). In the rest of the crystal relatively large inclusions were observed. Based on this finding we have been developing an annealing procedure with the goal of inclusion reduction without deteriorating the microstructure. Results of this activity will be presented in the next chapter.

Annealing of wafers

Due to the fact, that inclusions are present in many as grown crystal, a way how to decrease their size and density was looked for. The results of annealing of crystals No. 5 and 7 will be presented.

Crystal No.5 was grown at high Cd pressure. It contained large star shaped defects. We suppose these defects are Cd inclusions (Fig.4). The first annealing experiment was done in Cd vapors.

Annealing at Cd overpressure, 900/781°C

The star-shape corona started to be more transparent and the central part of inclusion was visible. However, the FWHM in rocking curves was drastically decreased.

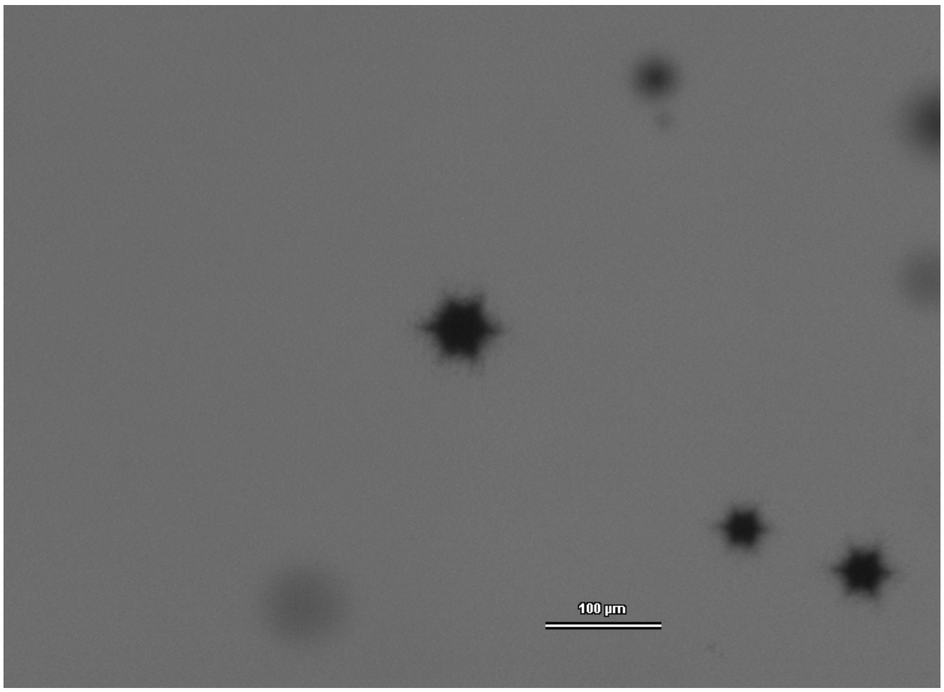


Fig.4 Wafer from crystal No.6 before annealing

Annealing experiments continued by annealing in Te vapors.

Annealing 600/523°C (Fig.5)

Temperature is not enough for elimination of visible Cd inclusions. However, reduction of large inclusions is clearly visible, where only central part of inclusions remained. IR transmission is bad. No change of FWHM in rocking curves was found.

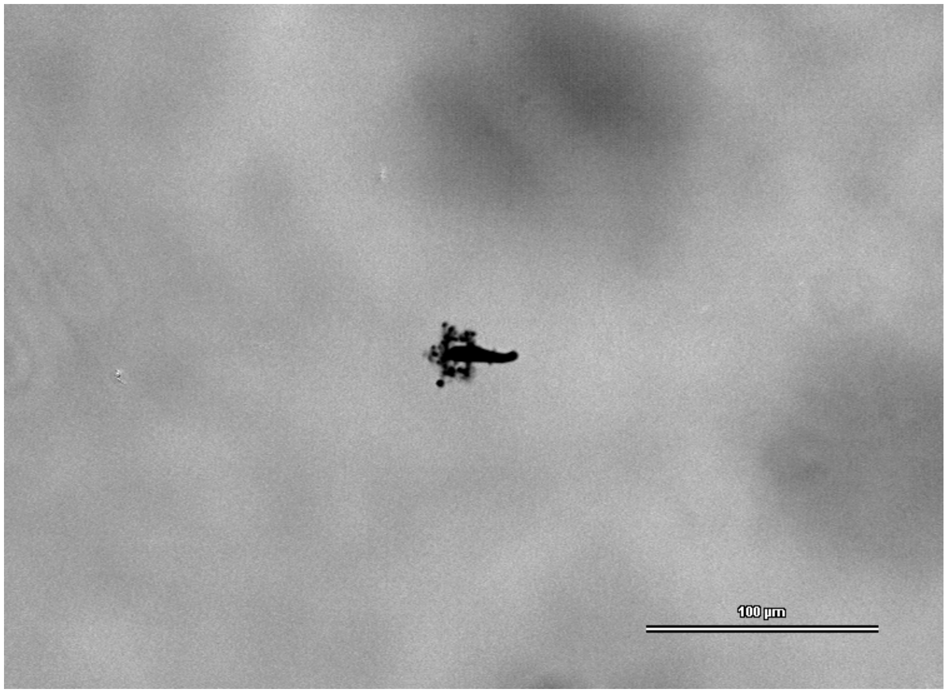


Fig.5. Wafer from crystal No.6 after annealing at 600°C

Annealing 850/734^{o}C (Fig.6)

Structure of inclusions was completely changed. Huge net of small inclusions (most probably Te rich) was created on dislocations. IR transmission is low. No change of FWHM in rocking curves was found.

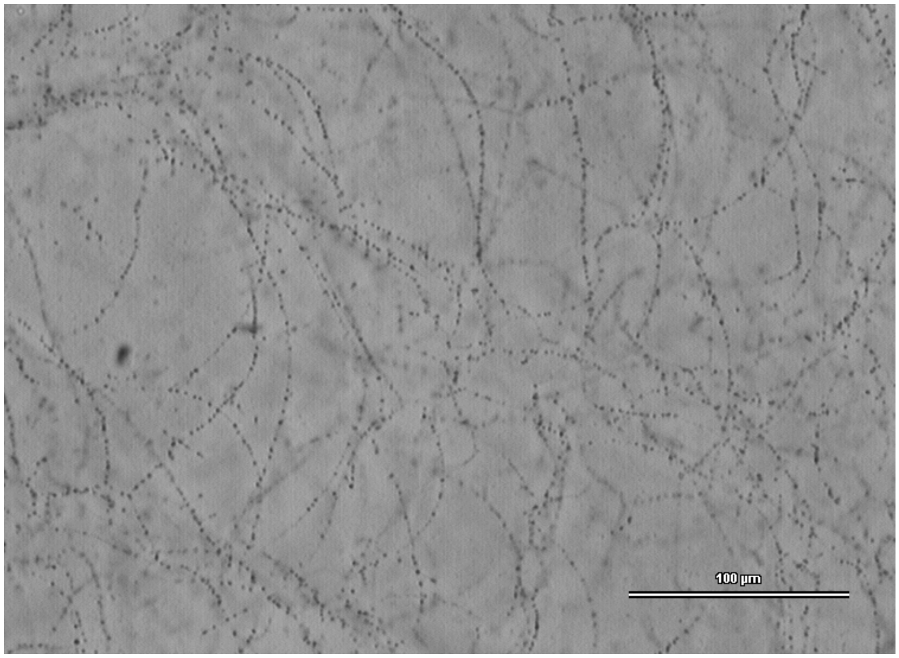


Fig.6 Crystal No.6 after annealing at 850°C in Te vapors.

Annealing 700/592^{o}C (Fig.7)

Temperature is enough for elimination of all Cd inclusions. Only small Te inclusions (~1-2um) were determined. No change of FWHM in rocking curves was found. IR transmission is low.

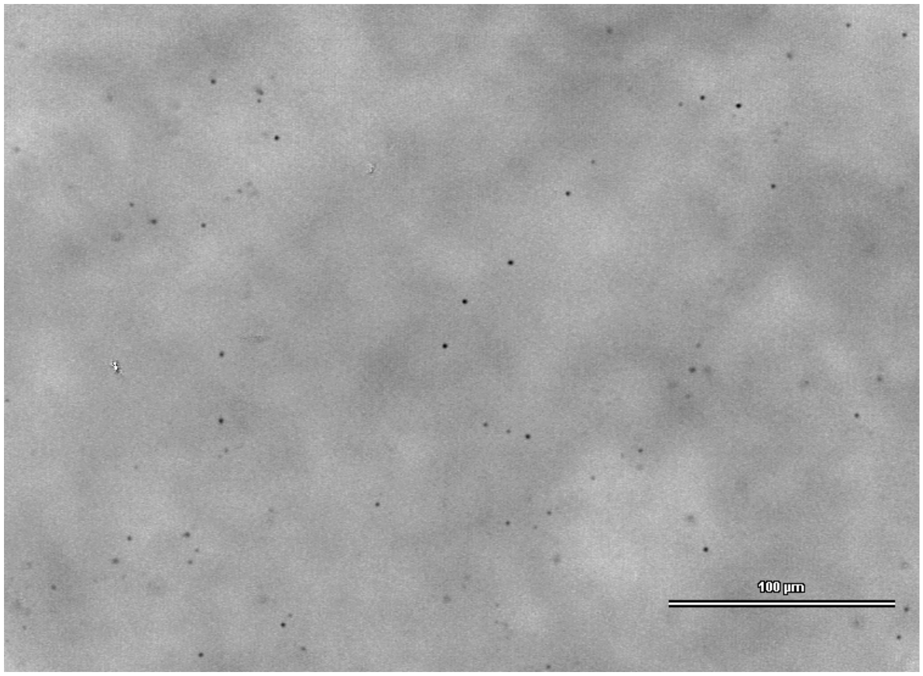


Fig.7 Crystal No.6 after annealing at 700°C in Te vapors

Optimum annealing conditions for crystals grown under high Cd pressure were found, which resulted in elimination of huge inclusions in as grown crystals. However, IR transmission after annealing is low probably due to formation of Cd vacancies under Te pressure. Reaching of high transmission would require an additional annealing step under Cd overpressure.

In the next part results of annealing of crystal No.7 prepared under low Cd pressure will be presented. The crystal was characterized by a high density of inclusions (more than $10^6/cm^2$). There were two types of inclusions in the samples. (Fig.8.) - triangular or hexagonal inclusions with diameter ~5-6um and non-regular inclusions with diameter ~1-2um. Also a very low IR transmission at 10um (20%) was observed in case of this as grown crystal (Fig.9.)

Inclusions were investigated by Inverse optical microscope Olympus IX70 with Pulnix CCD camera.

Two zone furnace was used for annealing. Samples were slowly cooled after annealing in the furnace.

Sample No.	Sample/Cd temperature [^oC]	Annealing time [Hours]
131A3E	as grown	
131A3G	600/500	24
131A3C	700/673	21
131A3K	699/588	20 (in Te pressure)

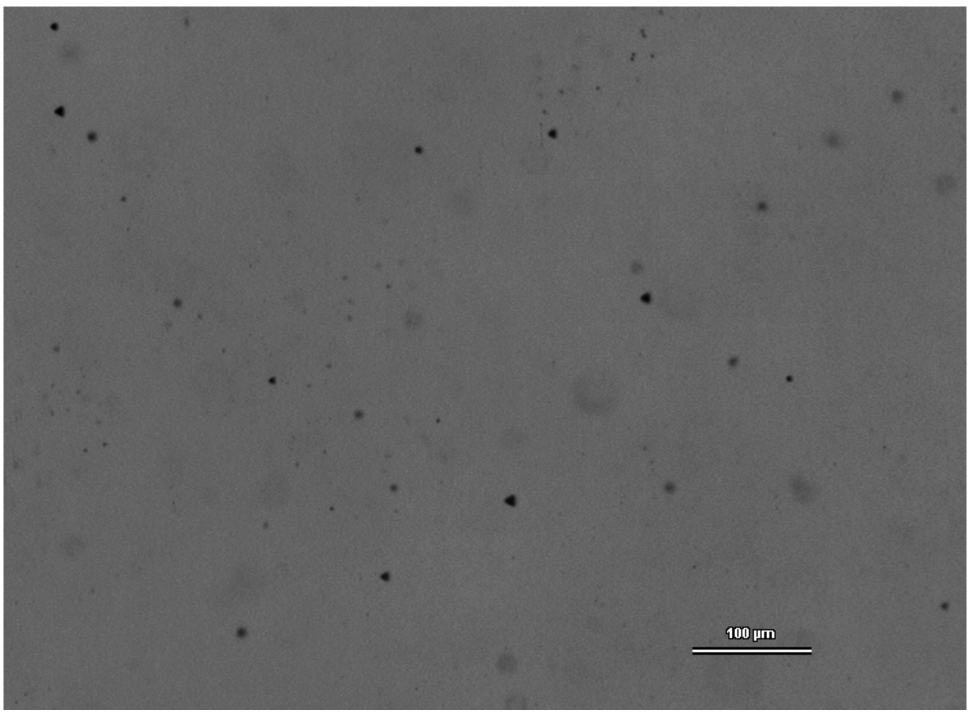


Fig.8 IR graph of sample 131A3Ea10a (crystal 7) – as grown

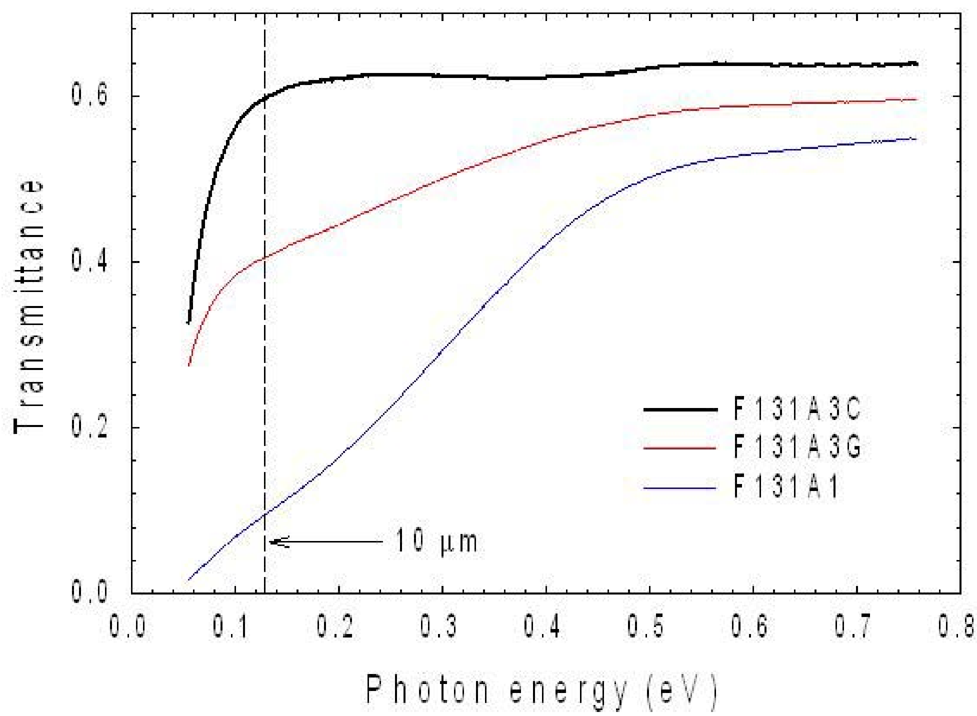


Fig.9 Transmission of crystal No.7 as grown (blue line) and after two different annealing steps (res and black line)

Several annealing conditions were tested: Properties after can ne described as follows:

Annealing 600/500^{o}C

Increase of IR transmission at 10um (to 40%) was observed (Fig.9). Visible Te inclusions (Fig.10) were not eliminated. From higher IR transmission we deduce, that only small Te inclusions (non distinguishable by IR microscope) were eliminated.

No change of FWHM of the rocking curves within the measurement precision was found.

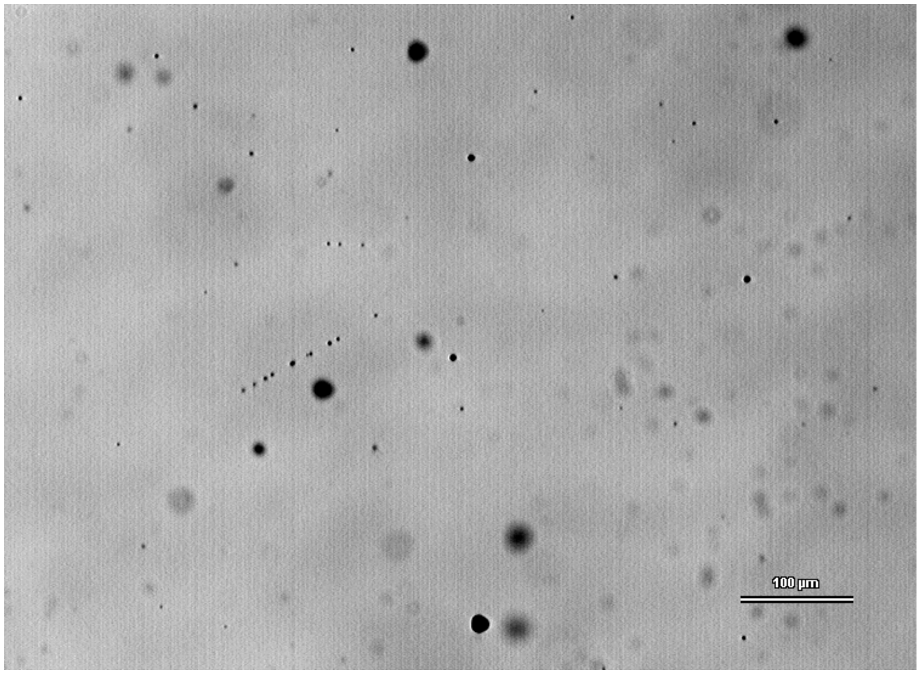


Fig.10 IR graph of crysatl No.7 after annealing at 600º

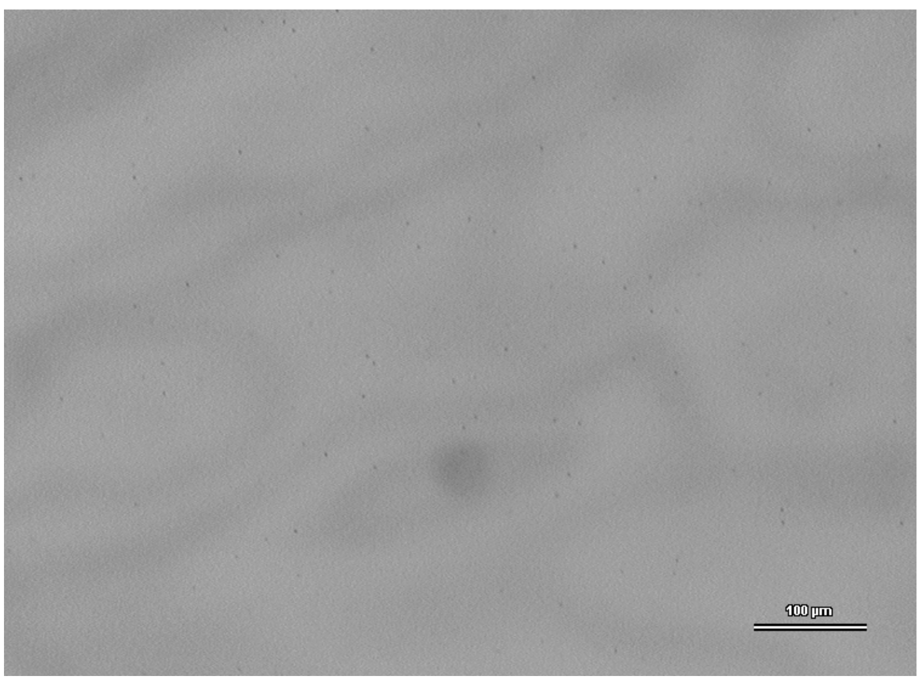


Fig.11 IR graph of crystal No.7 after annealing at 700º

Annealing 700/673^{o}C

The increase of IR transmission at 10um (60%) can be seen. (Fig.11). The temperature is enough for elimination of larger Te inclusions. Only low density of very small Te inclusions (~1um) was determined (Fig.7.). We cannot determine, whether remained inclusions are either at the same positions as large inclusions before annealing or they were created at different positions. The contrast of these inclusions in the IR microscope image was low comparing as grown one, therefore electronic image processing was used for contrast enhancement.
No change of FWHM in rocking curves was found.

Annealing at Te overpressure, 699/588^{o}C

No influence of annealing was found. The geometry (shape) of larger inclusions changed to more circular one (Fig.12.).

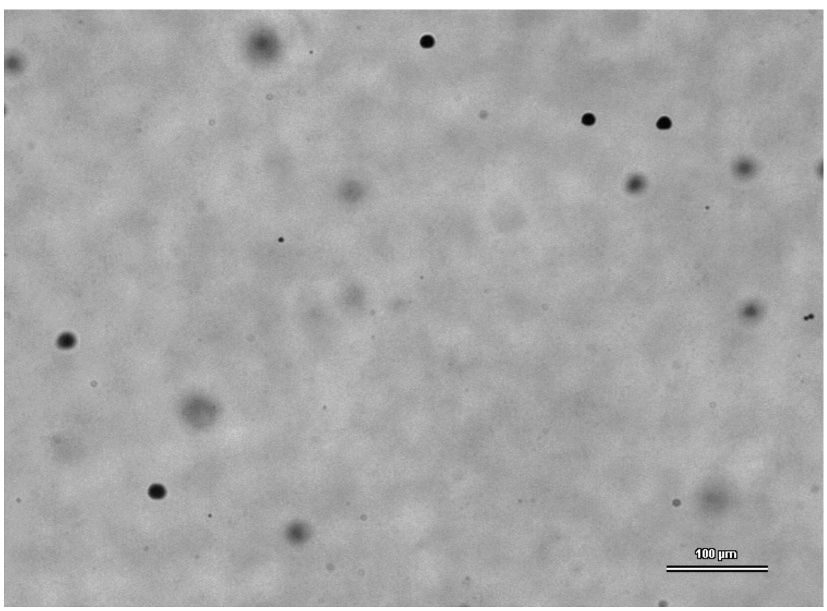


Fig.12 IR graph of crystal No.7 after annealing at Te overpressure

The annealing experiments can be summarized as follows:

Annealing conditions resulting in a substantial decrease of size of inclusions (to diameter ~1-2 μm) were found for crystals grown at high (~1.6atm) and low (~1atm) Cd pressure. Annealing under Te pressure (elimination of Cd inclusions in crystals grown at high Cd pressure) results, however, in low IR transmission and an additional annealing step at Cd pressure would be necessary to increase the transmission. Annealing under Cd pressure (elimination of Te inclusions in crystals grown under low Cd pressure) results in samples with good IR transmission.

Therefore, if annealing is necessary to improve properties of as grown crystals, it seems better to grow at low Cd pressure. If in future annealing steps will be introduced during the crystal growth and as grown crystals will be in most of the bulk inclusion free, then it is better to grow under high Cd pressure. The reason is, that high Cd pressure probbaly eliminates formation of Cd vacancies and other defects in Te sublattice and the IR trasnmission is high.

Study of FWHM of rocking curves

The standard double crystal diffractometer, which was used to analyze crystalline quality in the previos reports was broken for most of the contract period. Therefore we performed the measurements on other diffractometer, which has, however different measuring arrangement.

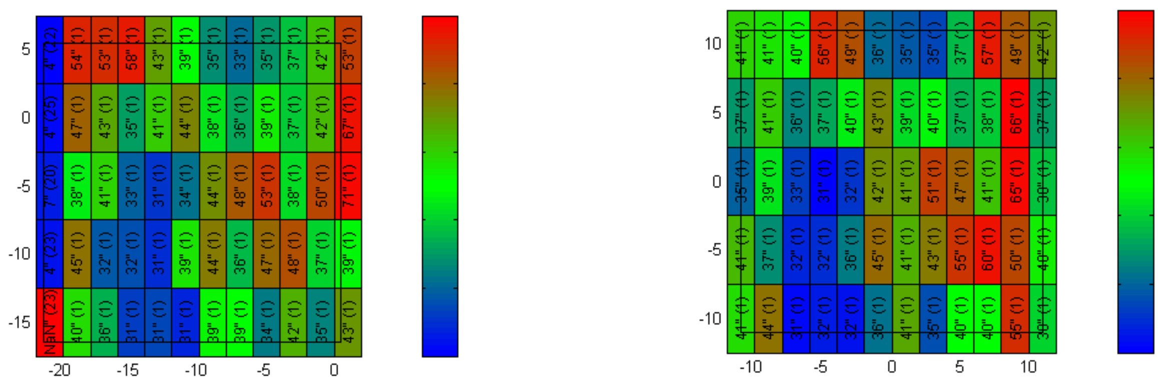
X-ray measurements were carried out by a Philips (PANalytical) X'Pert PRO MRD diffractometer with a high-resolution setup. The Cu radiation generated by a ceramic x-ray tube was collimated by a Göbel mirror and monochromatized by a four-crystal asymmetrical Ge(220) Bartels monochromator (asym. angle 15°, $CuK\alpha_1$ characteristic wavelength used). The incident beam was mainly limited by cross slits so that the size of the beam spot on the sample was (2 mm x 5 mm) for the symmetrical (224) CdZnTe diffraction. The axial divergence (in the direction perpendicular to the scattering plane) was also slightly reduced by Soller slits (0.02 rad). In this (pseudo-double crystal) setup with the Bartels monochromator and studied crystal as analyzer so called rocking curves were acquired.

This setup is advised for fast high resolution measurements at medium resolution. Hence measured FWHMs of diffraction lines can be larger than those achieved with more suitable

configurations. For example: we measure FWHM ≈ 26” for GaAs (004) reflection of GaAs(001) substrates and diffractometer producer inserts a FWHM ≤ 19” for Si (111) reflection of Si(111) sample.

Therefore the measured FWHM should be understood as approximate and measurement on a better setup should result in narrower FWHM.

Measurements of FWHM of wafers before and after annealing are presented on Figs.9 and 10. No substantial changes of crystal microstructure due to annealing can be seen.



(a) (b)

Fig. 9 FWHM of wafer 131A4 before and after annealing. Size of the spot 2x5mm^2

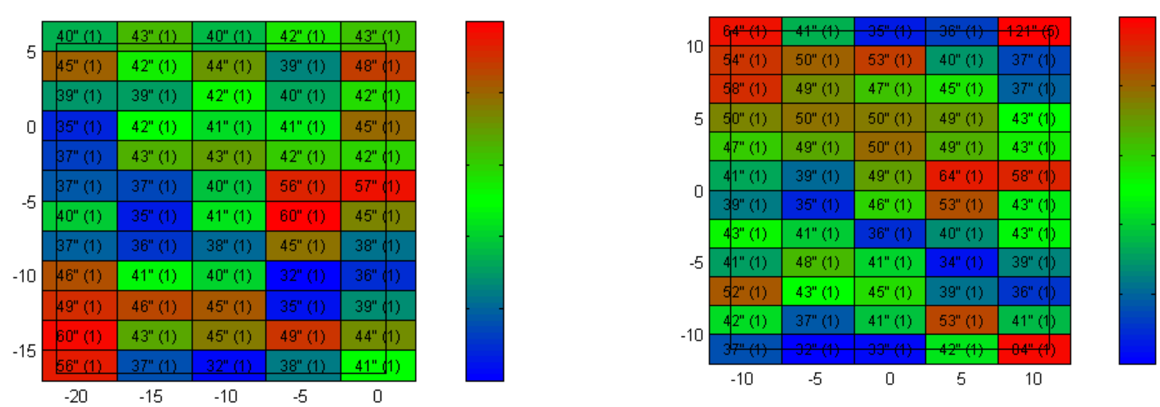


Fig. 10 FWHM of wafer 131A4 before and after annealing (perpendicular direction). Size of the spot 2x5mm^2

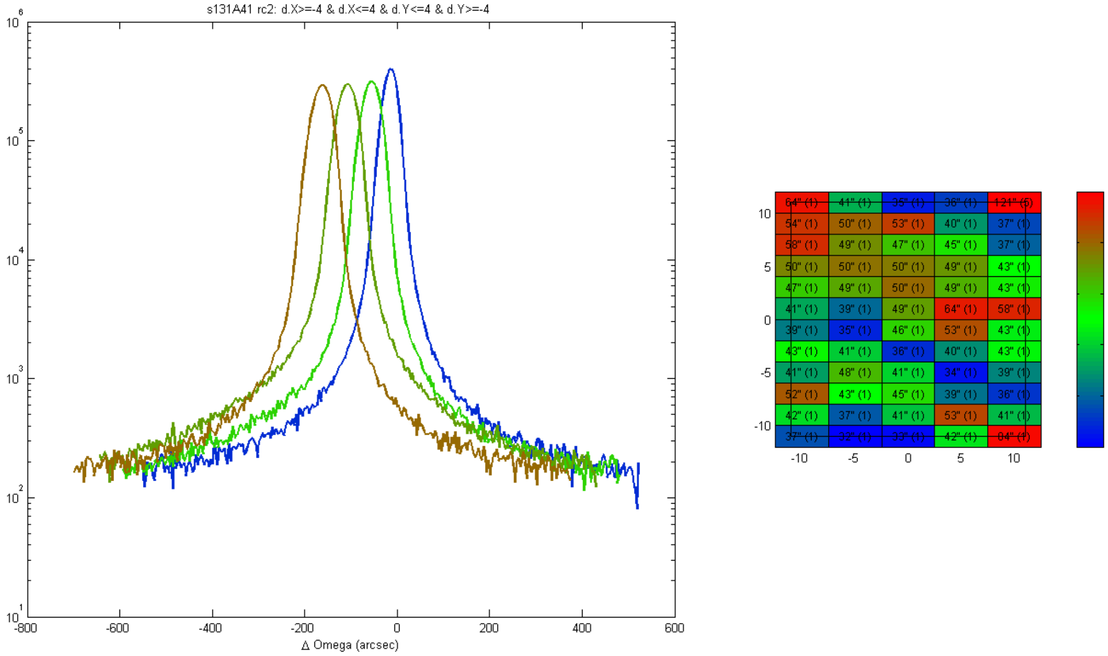


Fig.11 FWHM of rocking curves of wafer 131A4 after annealing. No split pekas were observed on the wafer.

Delivery of wafers

Two 2x2cm^2 wafers are delivered together with this report. Both wafers were annealed to remove inclusions. Results of annealing are demonstrated on Figs. 12 and 13

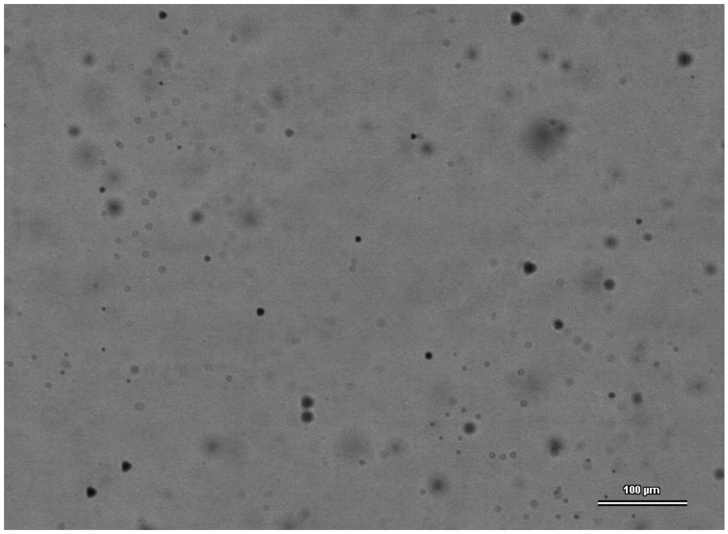


Fig.12 Crystal No.7 before annealing

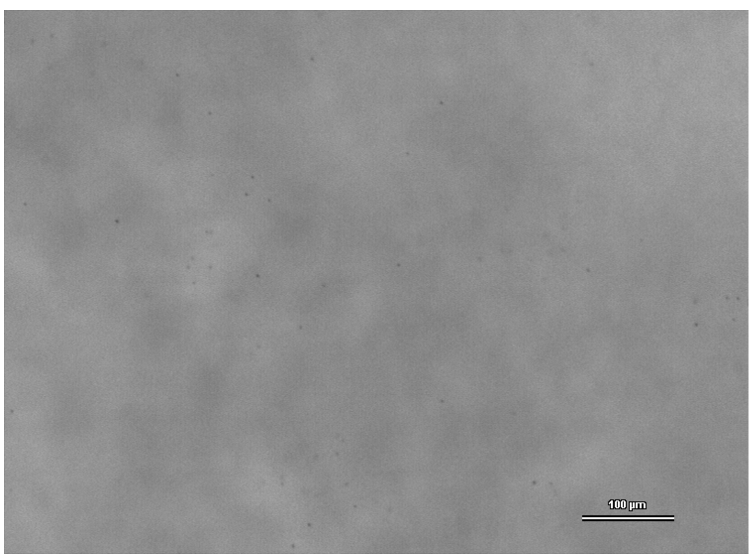


Fig.13 Crystal No.7 after annealing. The background white and black contrast is caused by scattering of light from surface , which was not completely flat. Small black spots represent atrefacts remaining after annealing.

Mechanical and chemical polishing of wafers was done by the way in detailed described in previous reports. The results can be considered as standard, i.e. with surface roughness 1-2nm measured by Zygo optical interferometer. Picture of surface after chemical polishing of the two delivered wafers can be seen on Figs. 14 and 15.

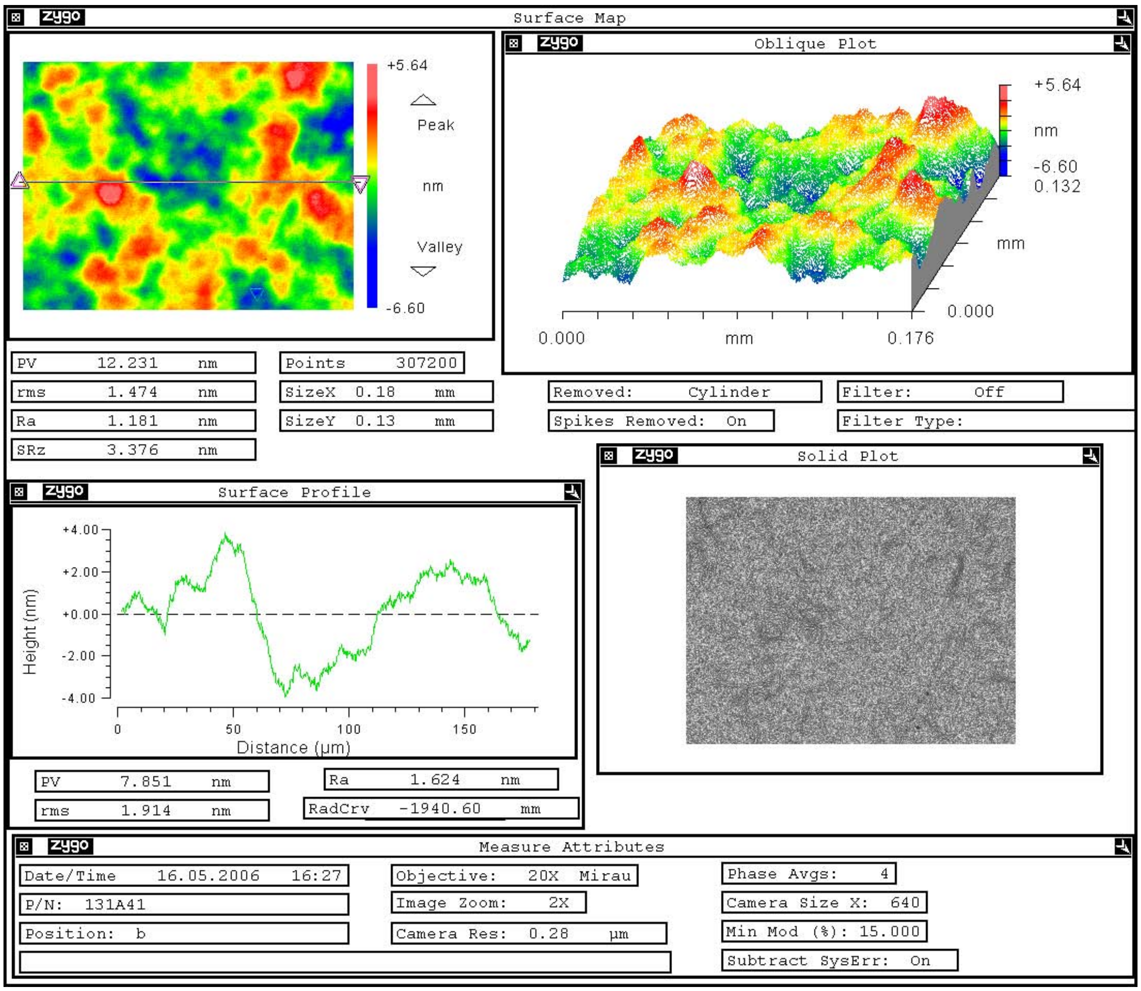


Fig.14 Surface of wafer 7-131b

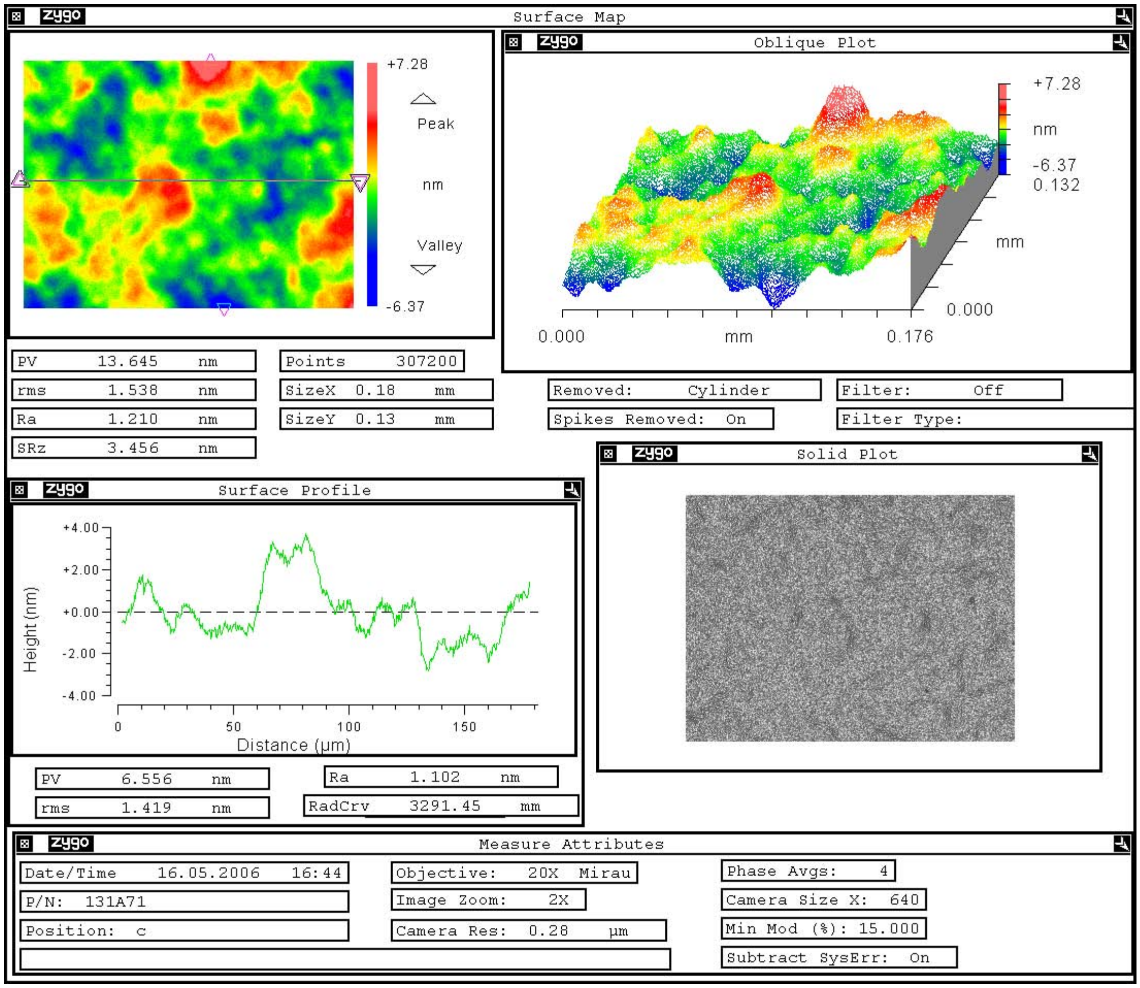


Fig. 15 Surface of wafer 131c after chemical polishing

Summary and outlook

The overall activity in crystal growth, substrate fabrication and surface polishing of last years done in the Institute of Physics, Faculty of Mathematics and Physics of Charles University can be summarized as follows

1. A complex middle pressure setup for crystal growth of large CZT boules under defined Cd pressure was constructed. Its construction was recently completed by a stabilized closed cycle water cooling system
2. The results of the growth are not satisfactory at the moment from the point of view of yield of the material suitable for substrate fabrication. There is a positive tendency in looking for optimal conditions, but this is not yet confirmed by repeating the growth runs under same conditions many times.
3. A succesfull annealing procedure resulting in substantial reduction of inclusions without influencing the crystal microstructure was developed. This will enable to use for substrate fabrication also boules, which had to be rejected, because inclusions were too large.
4. A complex substrate fabrication technology including orientation, cutting, mechanical and chemical polishing was developed. Surfaces with surface roughness 1-2nm can be obtained by a Br-methanol based etch. Several other etchants are under testing

The future plans depend on confirmation of experimental conditions resulting in achievement of a reasonable yield of material, from which substrates can be fabricated.. The Institute is ready to continue the effort based on internal funding for a certain time in order to receive data from a larger set of growth runs, than was possible within the last year. The time-scale of the effort is rather long. This is caused mainly by the size of the group, the existence of only one setup and a difficult and limited access to a number of technologies, which are necessary for substrate fabrication and testing (cutting machine, X-ray machine etc.

The Institute will provide NVESD the information about the results of the growth effort. We are also ready to consult any question concerning our activities with NVESD or other US institutions and companies.